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I, JONNE YABSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002950681 for a patent by CURTIN UNIVERSITY OF TECHNOLOGY and CORE LABORATORIES AUSTRALIA PTY LTD as filed on 12 August 2002.

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APPLICANT: CURTIN UNIVERSITY OF TECHNOLOGY and CORE LABORATORIES AUSTRALIA PTY LTD

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PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:

"IMPROVED PROCESS AND APPARATUS FOR PRODUCTION OF LNG BY REMOVAL OF FREEZABLE SOLIDS"

The invention is described in the following statement:-

IMPROVED PROCESS AND APPARATUS FOR PRODUCTION OF LNG BY REMOVAL OF FREEZABLE SOLIDS

Field of the Invention

This invention relates to a method and apparatus for continuously removing solids entrained within a liquefied natural gas (LNG) stream. Once removed, the solids can be converted to a liquid phase for ease of handling or recycling.

Background to the Invention

Natural gas contains a wide range of contaminant species which are capable of forming solids during the cryogenic process of liquefying natural gas. Such solids are referred to throughout this specification as "freezable solids". In a conventional LNG facility, pre-treatment of the natural gas is required to remove these contaminants prior to the liquefaction stage. Depending on the feed gas composition, pressure and temperature, these components are usually removed by various methods depending on the particular contaminant species involved. These conventional methods are both inefficient and expensive and particularly high in capital costs.

Of particular concern is the removal of CO_2 and BTEX from the natural gas feed stream in order to avoid formation of these solid components in the cold sections of the plant. Freezable solids which are not removed prior to liquefaction may precipitate and accumulate on the cold surfaces of heat exchangers and other plant equipment, eventually rendering these items inoperable. When fouling has reached a sufficient level, the equipment must be taken off-line for the fouling to be removed. In the process the equipment, baffles or pipework can be damaged which only encourages further fouling in the next production cycle. Moreover, freezable solids forming on metal surfaces may form an insulating film which reduces the thermal efficiency of the heat exchanger.

Cryogenic liquid-solid cyclones for removing solidified solid contaminants from LNG are not available commercially. There is a need for a more efficient and economical method and apparatus to remove freezable solids from LNG.

Throughout this specification the term "comprising" is used inclusively, in the sense that there may be other features and/or steps included in the invention not expressly defined or comprehended in the features or steps subsequently defined or described. What such other features and/or steps may include will be apparent from the specification read as a whole.

Summary of the Invention

According to one aspect of the present invention, there is provided an improved process for the production of LNG from a natural gas feed stream containing at least one contaminant species, the process comprising the steps of:

cooling said feed stream to produce LNG within a cooling vessel under conditions of pressure and temperature whereby at least one contaminant species forms freezable solids;

withdrawing an outlet stream comprising a mixture of LNG and said freezable solids from said cooling vessel;

transferring said outlet stream to a solids collection vessel in fluid communication with said cooling vessel; and

separating said freezable solids in the outlet stream from the LNG; whereby, at least one contaminant species is removed during production of LNG on a substantially continuous basis.

Preferably said process further comprises the step of heating said separated freezable solids to convert said freezable solids to liquid form. More preferably, said step of heating causes said substantially pure LNG to form a vapour and said vapour is recycled to said cooling vessel.

Preferably said step of cooling said feed stream includes the step of providing a stream of sub-cooled LNG to said cooling vessel. More preferably, said stream of sub-cooled LNG is recycled from the LNG produced in the cooling vessel. More preferably still, stream of sub-cooled LNG is provided by injecting said stream of sub-cooled LNG into said cooling vessel through an inlet adapted to be tangential to and located at a top portion of the cooling vessel to encourage the formation of a vortex within the cooling vessel.

Preferably, said step of transferring said outlet stream to said solids collection vessel includes the step of lifting said outlet stream to a level higher than the liquid level of LNG in the cooling vessel.

Preferably, said process includes the step of operating said solids collection vessel and said cooling vessel at a working pressure higher than the triple point pressure of the freezable solids.

Optionally, said process includes the step of substantially continuously removing said liquefied freezable solids from said solids collection unit.

Preferably, said at least one contaminant species is selected from the group comprising carbon dioxide, hydrogen sulphide, mercury, mercaptans and BTEX.

According to another aspect of the present invention, there is provided an apparatus for the production of LNG from a natural gas feed stream containing at least one contaminant species, the apparatus comprising:

a cooling vessel for cooling said feed stream to form LNG and freezable solids of at least one contaminant species;

means for withdrawing an outlet stream comprising a mixture of LNG and said freezable solids from said cooling vessel;

transfer means for transferring said outlet stream to a solids collection vessel in fluid communication with said cooling vessel; and

a solids collection vessel for separating said freezable solids from said LNG, said solids collection vessel being in fluid communication with said cooling vessel, said means for withdrawing an outlet stream and said transfer means whereby in uses said contaminant species are removed from said natural gas feed stream on a substantially continuous basis.

Preferably said means for withdrawing an outlet stream is arranged at a lower portion of said cooling vessel and said freezable solids migrate to said lower portion under the action of gravity. More preferably, said means for withdrawing an outlet stream creates a

vortex for increasing the gravitational migration of the freezable solids towards said lower portion.

Preferably, said solids collection vessel is heated to convert said freezable solids to liquid form for use in other areas of the plant or for ease of disposal.

Preferably, said cooling vessel is provided with an inlet to receive a stream of sub-cooled LNG which may be recycled from the LNG produced from the cooling vessel. More preferably still, said inlet is adapted to be tangential to and located at a top portion of the cooling vessel to encourage the formation of a vortex within the cooling vessel.

Preferably, said cooling vessel is constructed from a material having a low heat transfer coefficient to discourage formation of freezable solids on the cooling vessel itself.

Preferably, said transfer means is inclined at an angle to assist in the separation of the LNG from the freezable solids. More preferably, said transfer means is inclined at an angle not less than 60° to a horizontal reference plane. Preferably, said transfer means is driven by an external drive.

Preferably, said transfer means lifts the outlet stream to a level higher than the liquid level of LNG in the cooling vessel.

Preferably, the solids collection vessel and cooling vessel are arranged to operate at a working pressure higher than the triple point pressure of the freezable solids.

Optionally, said solids collection vessel is arranged to allow liquefied freezable solids to be removed from said solids collection unit in a substantially continuous operation.

Preferably, said solids collection unit is further adapted to allow said LNG vapour from said heated solids collection unit to be recycled to said cooling vessel.

Preferably, said at least one contaminant species is selected from the group comprising carbon dioxide, hydrogen sulphide, mercury, mercaptans and BTEX.

Brief Description of the Drawings

In order to facilitate a more comprehensive understanding of the nature of the invention, a preferred embodiment of the improved process and apparatus for production of LNG by removal of freezable solids will now be described in detail, by way of example only, with reference to the accompanying drawing in which:

Figure 1 is a schematic diagram of an apparatus in accordance with a first preferred embodiment of the present invention.

Detailed Description of the Preferred Embodiments of the Present Invention

According to the first preferred embodiment of the present invention, there is provided an apparatus 10 including a cooling vessel 12 adapted to include a hydrocyclone 14, a transfer means 36 and a solids collection vessel 42 in communication with each other.

A natural gas feed stream 16 is fed into the cooling vessel 12 via inlet 18. Prior to entering the cooling vessel 12, the feed stream 16 is typically dried to less than 50 parts per million of water. Any suitable process for drying the natural gas feed stream may be employed. One method of removing water from a natural gas feed stream is to use fixed-bed solid absorbents or other dehydration processes such as glycol or methanol. Another method of removing the water is to capture the water in gas/hydrate form. This method of removing water comprises cooling the natural gas by passing it over a cold surface at a temperature of $-15^{\circ}C$ sufficient to freeze the water molecules adjacent to the gas contact surface so that ice (hydrate) is deposited on the gas contact surface along the gas flow path.

The dried and pre-cooled natural gas feed stream 16 enters the vessel 12 through inlet 18. The pre-cooling conditions of the natural gas feed stream 16 need to be such that CO_2 and other contaminant species do not form solids upstream of the vessel 12. This is done by ensuring that the equipment upstream of the cooling vessel 12 is operated at above $-52^{\circ}C$.

One method of cooling the feed stream 16 is expansion through a JT valve 20 or other suitable expansion means located at the inlet 18 into the cooling vessel 12. As the

temperature drops in the cooling vessel 12 to between -100°C and -125°C, freezable solids of the contaminant species form. The process of cooling of the natural gas feed stream 16 may be enhanced by the addition of a recycle stream 22 through a second inlet 24. Depending on the degree of sub-cooling required, the circulating load of LNG to the recycle stream 22 may be many multiples of the amount required for customer use. The recycle stream 22 may be sub-cooled LNG or expanded natural gas.

A second recycle stream 23 may be injected into the cooling vessel 12 through a third inlet 25 adapted to be tangential to and located near a top portion of the cooling vessel 12. This arrangement has a result of generating a rotational velocity in the LNG inside the cooling vessel 12 in the form of a vortex.

The freezable solids of the contaminant species have a higher molecular weight than LNG and thus migrate under the action of gravity to a lower portion 26 of the cooling vessel 12. For example, the solid state density of CO_2 is about 1.2 grams per cm^3 compared with the density of LNG which is 0.44 grams per cm^3. Given that the solid state density of CO_2 is typically four times higher, CO_2 solids migrate to the lower portion 26 of the cooling vessel 12. The LNG towards the lower portion 26 of the vessel the LNG has a higher percentage dispersion of freezable solids of contaminant species than that closer to the liquid level 30. Purified LNG is withdrawn from a second outlet 28 of the cooling vessel 12. The second outlet 28 is located in an upper portion of the cooling vessel 12 . This LNG is essentially free of solids and can be used as the product supplied to a client or recycled to the cooling vessel 12 as recycle stream 22. The second outlet 28 should be located as close as practicable to the liquid level 30 to extract LNG with a minimum of freezable solids.

If the purified LNG includes solids, separation of these solids may be required. Multiple cascaded separators may be required to provide the degree of separation needed. Such additional separators may be provided either in series or in parallel.

Testing was conducted at Curtin University of Technology using a Sapphire Cell as the cooling vessel 12. The Sapphire Cell makes it possible to view the manner in which CO_2 and other freezable solids form inside the cell. Testing using a conducted high-speed

vortex system provided with the Cell has shown that the CO_2 that is present in the LNG is in the form of fine solid particles. The particles are typically within the range of 10 to 100 μm with a significant percentage having a particle diameter of about 20 to 30 μm, especially when the feed gas has a "low" CO_2 content less than 2%. It has been observed that the solidifying CO_2 particles stick to each other and the thickness of the particle would render conventional cyclones ineffective. Without wishing to be bound by theory, it is believed that these small particles serve as nucleation sites or seed crystals for further precipitation and growth of CO_2 and other freezable solids. It is believed that this contributes to the efficiency and reaction yield of the cooling vessel which is in effect a form of a fluidised bed reactor.

The lower portion of the cooling vessel 12 has an integral hydrocyclone 14. An outlet stream of LNG plus freezable solids 32 is continuously removed from the cooling vessel 12 via integral hydrocyclone 14 and is carried from the cooling vessel 12 via a transfer means 36 to a solids collection vessel 42. The solids collection vessel 42 and cooling vessel 12 must be in fluid communication to facilitate continuous removal of the solids.

The hydrocyclone 14 located at the lower portion 26 of the cooling vessel 12 dramatically increases the rate of settling of the freezable solids within the LNG in the cooling vessel 12. The inclusion of the hydrocyclone 14 thus enables a smaller cooling vessel 12 to be used than would otherwise be required, relying on gravity separation alone, and increases the quality of the separation. It is to be clearly understood, however, that migration to the lower portion 26 of the cooling vessel 12 may occur by gravity only. A solids separation means other than a hydrocyclone can be used to withdraw the freezable solids from the cooling vessel 12. In an alternative embodiment, the natural gas feed stream 16 may be injected below the surface of the liquid level of the LNG within the cooling vessel 12. When natural gas feed stream 16 is injected below the level of LNG in the cooling vessel 12, bubbles of natural gas form providing an increased surface area for heat transfer. The LNG extraction outlet 28 may need to be relocated to a point higher in the cooling vessel 12 to ensure that this LNG is as free of entrained solids as possible.

In a preferred embodiment of the present invention, the transfer means 36 is an auger or

screw conveyor driven externally or internally by a direct shaft 38. If the drive of the transfer means is internal, the motor and gearbox would be subjected to continuous exposure to pressurised LNG and rotating seals may not be used. Given that reliability of rotating equipment at cryogenic temperatures is generally poor, an extended shaft and casing may be preferred to allow the motor to be warmed. Alternatively an external drive may be provided such that the motor, gearbox and seal can be located on an extended shaft under warmer conditions. The seal will need to withstand the same working pressure as that of the cooling vessel 12.

The screw conveyor 36 is mounted at an angle to assist in the draining of the LNG from the outlet stream 32. Typically the angle of inclination of the screw conveyor 36 will be in the order of 60°, however the exact angle of inclination of the screw conveyor 36 is not critical to the present invention. The outlet stream 32 is carried by the screw conveyor 36 to a level 37 that is higher than the liquid level 30 in the cooling vessel 12. It is envisaged that the capillary action of having level 37 above the liquid level 30 of the LNG in the cooling vessel 12 encourages the LNG to drain from the outlet stream 32, leaving behind a solid slush 40. The slush 40 is collected in a solids collection vessel 42 which is preferably heated to transform the collected freezable solids back to liquid form. An example of a suitable solids collector vessel is a reboiler.

The cooling vessel 12 and the solids collection vessel 42 are in fluid communication such that the operating pressure in the cooling vessel 12 and the pressure within the solids collection vessel 42 are kept at equilibrium. The working pressure of the solids collection vessel 42 should be higher than the triple point pressure of the freezable solids. In the case of CO_2, the triple point pressure is in the order of 75 psia. In normal operation, the cooling vessel would operate at around 200 psia. If the contaminant freezable solids were melted at pressures below the triple point pressure vapour would be produced. Given that the LNG cooling vessel, the transfer means and the solid collections unit are in fluid communication, each of these units will need to be designed to withstand the same working pressure.

The screw conveyor 36 may be combined with a rotating roller (not shown) at the exit of the hydrocyclone 14. The rotating roller creates a seal between the cooling vessel 12 and

the solids collection vessel 42. The slush 40 collected in the solid collection vessel 42 may be heated by means of introducing a cool recovery stream.

Typically the screw conveyor 36 would be clearance fit in a casing 44 to allow space for the draining LNG. It may be possible to construct an auger to be off-centre to give the least clearance on the solid side while allowing plenty of space for returning LNG on the other side. A bushing or bearing or other suitable rotation control means would need to be provided at the top and bottom of the screw conveyor 36 to control its rotation and end thrust. The bottom bearing would be blind such that the screw conveyor 36 is sealed at the bottom. Once the solids are collected in the collection vessel and are converted to a liquid, the liquid contaminant species may be discharged through an outlet 46 and either circulated through the system for heat recovery or, preferably, reinjected back into, for example, a disposal well, taking advantage of the pressure build-up in the disposal well due to vaporisation.

The LNG is driven off as a natural gas vapour during heating of the slush 40 in the reboiler 42. To minimise the natural gas recycling loop through inlet 52, it is important to have as much liquid as possible drain from these collected solids prior to the solids being deposited in the solids collection vessel. This natural gas vapour stream 50 may be returned to the cooling vessel 12 via inlet 52. The liquefied freezable solids are discharged from the reboiler at outlet 46. The discharge of the freezable solids can either be in a continuous operation or a batch operation controlled by the level of the slurry in the reboiler 42.

It is preferable for the reboiler to be provided with an electric heating unit to conduct the warming. The heating unit would be controlled by a thermostat to control the temperature to provide liquid CO_2 or other liquids of the solid contaminants at the chosen working pressure. For CO_2 at the nominal working pressure of 200 psia the thermostat would be set to –30°C. The heating system would have to have enough surface area to gently warm the mixture of solids and liquefied natural gas without creating hot spots. If required, a stirring system can be employed to keep the mixture at a uniform temperature.

It is envisaged that the discharged liquid contaminant species, and in particular CO_2, may

be used to advantage for other heat exchangers required in other sections of an LNG plant or indeed for seabed coil tubing heat exchangers to heat liquid CO_2 to vapour/supercritical and use the generated vapour pressure for self-injection into disposal wells, aquifers or reservoirs. A seabed heat exchanger using liquid CO_2 through a pipeline is a simple thing to design and install and saves energy, time and money when compared to re-compression or venting costs.

The contaminant species of greatest interest to operators of LNG plants is CO_2. However, other contaminant species are suitable for continuous removal and collection according to the present invention. In particular hydrogen sulphide (H_2S) has a freezing point for pure H_2S of 82.9°C at 14.5 psia and a vapour pressure of 271 psia at 20°C. If the H_2S is present in the initial feed mixture it would solidify in the cooling vessel in the same way as described above. The freezable solids of H_2S would be collected in the usual way through the hydrocyclone 14 and transferred by means of the screw conveyor 36 to the solids collection vessel 42. The discharge from the solids collection vessel 42 would include both CO_2 and H_2S and this stream may be introduced into a second separator (not shown) to separate CO_2 from the H_2S. The second separator or column would be operated under conditions which are sufficient to produce an overhead stream rich in CO_2 and a bottoms stream enriched in H_2S.

Another contaminant species of interest is mercury which is often found in natural gas fields throughout the world in various concentrations. Even very low amounts of mercury in gas feed cryogenic process plants cause corrosion in aluminium alloy equipment. Mercury-induced corrosion, particularly in the presence of water, has been known for some time, but the specific corrosion mechanism is not fully understood. Mercury removal from the feed gas is therefore the only currently available remedy for the problem.

It is known that when gas containing mercury is cooled to -12°C at a pressure of 1058.5 psia, the mercury condenses out as a solid. It is thus reasonable to assume that mercury would be one of the contaminant species capable of forming a freezable solid.

A suitable vessel for use as the cooling vessel 12 in accordance with the present invention

would be a vessel of the type disclosed in the applicant's Australian Provisional Patent Application No. PS0021. In that application, a cooling vessel for LNG liquefaction constructed from a material having a low thermal conductivity was disclosed. It was found that using such a material, the freezable solids of the contaminant species formed preferentially away from the walls of the cooling vessel. The cooling vessel as disclosed in Australian Associated Provisional Patent No. PS0021 could be modified at its lower portion to include a hydrocyclone 14 plus transfer means 36.

Tests were conducted on a feed gas containing 25% CO_2 introduced at 280 psia and −140°C. Using the method described above, the CO_2 content was reduced from 25% to 0.29%. The feed gas contained the following:

Component	**Mole Fraction**
N_2	1.939
CO_2	24.95
C1	64.64
C2	5.493
C3	2.385
IC_4	0.239
NC_4	0.292
IC_5	0.038
NC_{5+}	0.023

Note: The gas includes parts per million amounts of mercaptans.

After testing, the GC analysis of the LNG produced following separation of the solid contaminants at 145 psia and −140°C reads as follows:

Component	Mole Fraction
N_2	1.28
CO_2	0.29
C1	94.65
C2	4.48
C3	2.02
IC_4	0.21
NC_4	0.27
IC_5	0.04
NC_{5+}	0.03

The mole fraction of CO_2 has been reduced substantially from 24.95% in the feed stream to only 0.29% in the LNG outlet stream. The solids collected had the following composition:

Component	Mole Percentage
CO_2	95.37
C1	0.37
C2	0.06
C3	0.66
IC_4	0.90
NC_4	1.92
IC_5	0.36
NC_5	0.24
C6	0.11

Now that an embodiment of the present invention has been described in detail, it will be apparent to those skilled in the relevant arts that numerous modifications and variations may be made without departing from the basic inventive concepts. In particular, whilst accommodation of a hydrocyclone fitted to the bottom of the vessel in combination with an inclined auger and reboiler have been described in the preferred embodiment of the

present invention, other means for removing the solids from the bottom of the vessel and separating the solids may be used and equally fall within the scope of the present invention. For example, a rotating high gravity separator in the form of a centrifuge may be provided for continuous separation of the liquid/solid mixture. The solid/liquid separation may then be achieved using filtration; for example, by means of a particle trap provided with the rotary scraper. All such variations and modifications are to be considered within the scope of the present invention, the nature of which is to be determined from the foregoing description.

DATED this 11th day of June 2002

CURTIN UNIVERSITY OF TECHNOLOGY and CORE LABORATORIES AUSTRALIA PTY LTD

By Its Patent Attorneys

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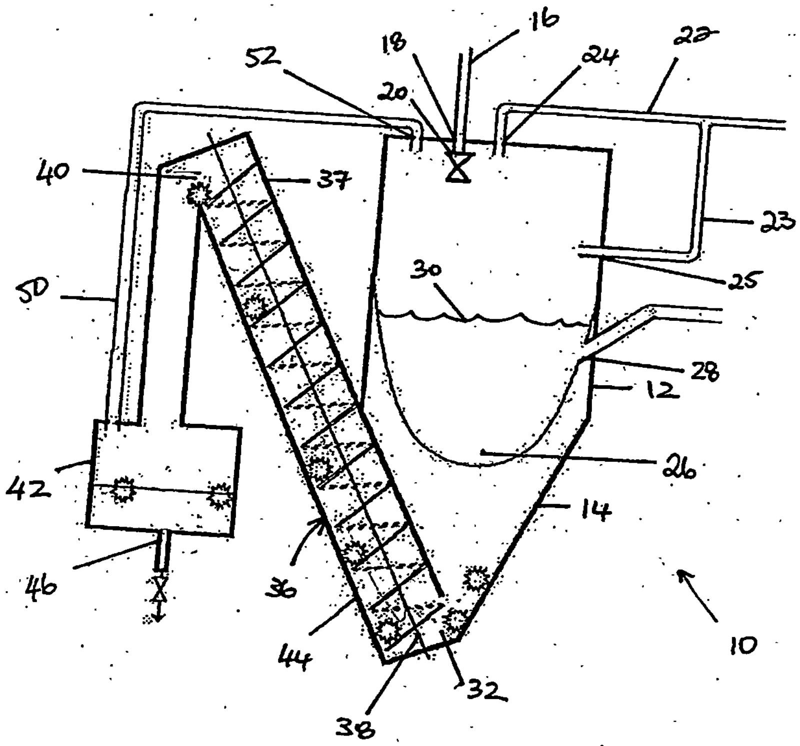

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